(12) UK Patent Application (19) GB (11) 2 308 358 (13) A

(43) Date of A Publication 25.06.1997

(21) Application No 9622136.1

(22) Date of Filing 24.10.1996

(30) Priority Data
(31) 9526262 (32) 21.12.1995 (33) GB

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(51) INT CL[6]
C22B 3/26 // C22B 11:00 15:00 34:32 60:02 60:04

(52) UK CL (Edition O)
C1A AG10 AG11 AG25 AG29 AG36 AG57 APD2B AP21 A321 A322

(56) Documents Cited
US 4486391 A

(58) Field of Search
UK CL (Edition O) C1A APD2B APD2S APD2Y AP21 AP36 AP37 AP38
INT CL[6] C22B 3/26
ONLINE: WPI

(54) Recovering metal values by solvent extraction

(57) A process for extracting a metal in ionic form from a solid or liquid material in which it is contained comprises the steps of (1) contacting the material with a metal complexing agent to sequester the metal ions and with a solvent to dissolve the metal complex that forms, and (2) separating the solvent liquor containing the metal complex from the material. The solvent comprises at least one fluorine containing compound selected from the (hydro)fluorocarbons and the (hydro)fluorocarbon ethers.

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EXTRACTION PROCESS

The present invention relates to the extraction of metals in ionic form from materials containing them using a solvent extraction technique in which a solvent is used to extract the metal ions as their organic complexes.

Processes for extracting metals in ionic form from crude or raw materials containing them using a suitable organic solvent are known in the art. In these known extraction processes, the crude or raw material is contacted, usually with mixing, with both a metal complexing agent and an organic solvent which is capable of dissolving the complexing agent. The complexing agent serves to sequester the metal ions while the organic solvent dissolves the metal complex that forms. The solvent liquor containing the metal complex is then separated from the crude or raw material for subsequent processing, e.g. to isolate and recover the metal. The extraction of metals using the above described technique is exploited industrially to extract copper from the dilute aqueous solutions which are formed during the processing of the ore and in the purification of uranium and other metals obtained in the processing of nuclear fuel. High boiling solvents such as kerosine are typically used in the process.

The present invention provides a new solvent based metal extraction process which can be used to extract a wide variety of metals in ionic form from the materials in which they are contained.

According to one aspect of the present invention there is provided a process for extracting a metal in ionic form from a material in which it is contained which process comprises the steps of (1) contacting the material with a metal complexing agent to sequester the metal ions and with a solvent to dissolve the metal complex that forms, and (2) separating the solvent liquor containing the metal

According to a further aspect of the present invention there is provided a process for extracting metal ions from a material in which they are contained which process comprises adding a metal complexing agent to the material to form a metal complex between the ions and the complexing agent and extracting the metal complex so formed from the material as a solution in a solvent, wherein the solvent comprises at least one fluorine containing compound selected from the (hydro)fluorocarbons and the (hydro)fluorocarbon ethers.

The present invention also provides for the use of a solvent comprising at least one fluorine containing compound selected from the (hydro)fluorocarbons and the (hydro)fluorocarbon ethers to extract metal ions as their organic complexes.

In the process of the present invention the metal containing material is treated with both a metal complexing agent and an extraction solvent which is capable of dissolving the complexing agent. The metal complexing agent serves to sequester the metal ions while the solvent dissolves the metal complex that forms. The process will ordinarily be conducted under reasonably vigorous mixing conditions so as to facilitate the formation of the metal complex and the dissolution of this complex into the solvent. The solvent liquor containing the metal complex can then be separated from the material for subsequent processing, e.g. to isolate and recover the metal. Acids may be used to strip the metal from the solvent liquor. Where the material to be subjected to the extraction is an aqueous medium, it will often be necessary to wait for the organic and aqueous components to phase separate before isolating the solvent liquor.

The addition of the metal complexing agent and the solvent to the material to be extracted may be carried out sequentially with either the complexing agent or the solvent being added first. Alternatively, the complexing agent and the solvent may be added at the same time, either as separate reagents or as a single reagent by dissolving the complexing agent in the solvent prior to use.

The metal complex which is formed between the metal ions and the metal complexing agent may itself carry a positive or even a negative electrostatic charge but will preferably be electrostatically neutral.

The process of the present invention may be used to extract metals in ionic form from solid or aqueous media. Where the process is used to extract a metal from an aqueous medium, this medium may be the result of earlier processing. For example, where the metal to be extracted is bound in a solid matrix it may be desirable or even necessary to solubilise the solid material in an aqueous medium with the aid of an aggressive reagent such as concentrated nitric acid or aqua regia (a blend of concentrated nitric and sulphuric acids) prior to performing the metal extraction process of the invention.

The solvent which is used in the process comprises at least one fluorine containing compound selected from the (hydro)fluorocarbons and the (hydro)fluorocarbon ethers. In this specification, a (hydro)fluorocarbon is a compound selected from the group consisting of the hydrofluorocarbons and the perfluorocarbons and a (hydro)fluorocarbon ether is a compound selected from the group consisting of the hydrofluorocarbon ethers and the perfluorocarbon ethers. The solvent may contain a mixture of two or more fluorine containing compounds, including a mixture containing a (hydro)fluorocarbon and a (hydro)fluorocarbon ether.

Suitable (hydro)fluorocarbons and (hydro)fluorocarbon ethers for the solvent will typically have a boiling point in the range of from -85 to 120°C. Preferably, the (hydro)fluorocarbons and (hydro)fluorocarbon ethers from which the one or more fluorine containing compounds making up the solvent are selected will have a boiling point in the range of from -55 to 60°C, more preferably in the range of from -55 to 25°C. Particularly preferred (hydro)fluorocarbons and (hydro)fluorocarbon ethers for the solvent will have a boiling point of 0°C or below, for example in the range of from -55 to 0°C.

The advantage of using low boiling (hydro)fluorocarbons and (hydro)fluorocarbon ethers is that the removal of such solvents is

relatively facile and can be accomplished by flash evaporation at relatively low temperatures, e.g. room temperature and below.

The preferred solvents comprise one or more fluorine containing compounds selected from the hydrofluorocarbons and the hydrofluorocarbon ethers and, of these, solvents comprising one or more hydrofluorocarbons are particularly preferred.

The preferred hydrofluorocarbon ethers are those having from 2 to 4 carbon atoms, with the fluorine containing dialkyl ethers having from 2 to 4 carbon atoms being particularly preferred and the fluorine containing dimethyl ethers being especially preferred. Examples of C_{2-4} hydrofluorocarbon ethers which may be used for the solvent include, inter alia, trifluoromethyl difluoromethyl ether (CF_3OCF_2H), trifluoromethyl fluoromethyl ether (CF_3OCFH_2), bis(difluoromethyl) ether (CF_2HOCF_2H), trifluoromethyl methyl ether (CF_3OCH_3), pentafluoroethyl difluoromethyl ether ($CF_3CF_2OCF_2H$), 1,1,1,2-tetrafluoroethyl trifluoromethyl ether ($CF_3CFHOCF_3$), pentafluoroethyl methyl ether ($CF_3CF_2OCH_3$) and 1,1,2,2-tetrafluoroethyl trifluoromethyl ether ($CF_2HCF_2OCF_3$).

The preferred hydrofluorocarbons for use in the solvent are selected from the C_{1-3} hydrofluorocarbons and particularly the C_{1-3} hydrofluoroalkanes. Examples of C_{1-3} hydrofluoroalkanes which may be used include, inter alia, trifluoromethane, fluoromethane, difluoromethane, pentafluoroethane, 1,1,1-trifluoroethane, 1,1,2,2-tetrafluoroethane, 1,1,1,2-tetrafluoroethane, 1,1,1,2,2,3-hexafluoropropane and 1,1,1,3,3,3-hexafluoropropane. Solvents comprising one or more compounds selected from the hydrofluoromethanes or the hydrofluoroethanes are particularly preferred and, of these, solvents comprising 1,1,1,2-tetrafluoroethane (R-134a) are especially preferred.

A fluorine free co-solvent may be blended with the one or more fluorine containing compounds specified above in order to modify their solvent properties. Co-solvents having a boiling point of 100°C or below are preferred with particularly preferred co-solvents being selected from the hydrocarbons which have a boiling point of 25°C or

below, for example in the range of from -55 to 25°C. Where a co-solvent is used, it will preferably have a boiling point which is similar to that of the fluorine containing compound, e.g. within ±20°C of the boiling point of the fluorine containing compound.

The solvent which is used must, of course, be in liquid form. Where the solvent comprises one or more low boiling compounds which are gases at room temperature, the required liquid form may be attained by cooling the solvent to a suitably low temperature prior to use or by pressurising the container in which the metal extraction process is to be carried out.

The type of complexing agent which is used in the process will be determined by the type of metal which is to be extracted. However, the complexing agent should contain groups that promote the solubility thereof in the solvent which is to be used and if the material which is to be subjected to the extraction is an aqueous medium, then the complexing agent will preferably also contain groups which reduce the solubility thereof in aqueous media. Of course, the same groups could perform the dual function of promoting solubility in the solvent and reducing solubility in aqueous media. Suitable dual function groups may include alkyl, which may be partially or fully fluorinated, keto, ester, ether, carboxylate, amino, amido, hydroxylamino, phosphine oxide, oxysulphur and aromatic groups and oxyphosphorous anions and their esters.

Examples of complexing agents which can be used in the process of the present invention include compounds having the following formulae:

(1) $RCOCH_2COR^1$

(2) $RCOCHFCOR^1$

(3) $RCOCHR^2COR^1$

(4) RCO_2H

where

R is an alkyl group, a perfluoroalkyl group, a group having the formula $H(CF_2)_n-$, where n is 1 to 12, or a group having the formula $H(CF_2CHF)_m-$, where m is 1 to 20;

R^1 is an alkyl group, a perfluoroalkyl group, a group having the formula $H(CF_2)_n-$, where n is 1 to 12, or a group having the formula $H(CF_2CHF)_m-$, where m is 1 to 20; and

R^2 is a partially or fully fluorinated alkyl group.

Other suitable complexing agents which may be used in the process of the present invention include the macrocyclic complexing agents containing several heteroatoms such as oxygen and nitrogen which have the ability to form dative-covalent bonds with metal ions. Such complexing agents include the crown ethers which contain several oxygen atoms such as dicyclohexyl-18-crown-6, dibenzo-12-crown-4 and 18-crown-6, and the cryptands which contain a combination of heteroatoms such as cryptand 222.

Suitable complexing agents may also be selected from the organo-phosphorous compounds such as the organo-phosphates and organo-phosphines and the organo-nitrogen compounds such as the amines, amides and oximes. Still further complexing agents may be selected from the ketones, ethers and glycols.

The process of the present invention may be used to extract metals such as copper and uranium from the aqueous solutions formed during the processing of their ores. The process may also be used to extract uranium and other metals such as plutonium and the various fission products during the reprocessing of spent nuclear fuel rods. Further uses for the process include the extraction of toxic metals such as chromium from aqueous solutions generated during chemical processes, the extraction of metals from spent catalysts, e.g. palladium from charcoal, and the extraction of heavy metals from contaminated soils.

The present invention is now illustrated but not limited with reference to the following example.

Example 1

In this example the solubility of ruthenium (III) tris[2,4-acetylacetonate] ($Ru(acac)_3$) in liquid 1,1,1,2-tetrafluoroethane (R-134a) was investigated.

The solid $Ru(acac)_3$ was placed in a glass pressure bottle and the R-134a was then introduced in 3 to 5 g additions from an aerosol can. After each R-134a addition the bottle was shaken to facilitate dissolution of the $Ru(acac)_3$ in the R-134a. 33.8 g of R-134a were needed to dissolve all the solid giving a solubility of 0.53g per 100g R-134a.

Claims:

1. A process for extracting a metal in ionic form from a material in which it is contained which process comprises the steps of (1) contacting the material with a metal complexing agent to sequester the metal ions and with a solvent to dissolve the metal complex that forms, and (2) separating the solvent liquor containing the metal complex from the material, wherein the solvent comprises at least one fluorine containing compound selected from the (hydro)fluorocarbons and the (hydro)fluorocarbon ethers.

2. A process for extracting metal ions from a material in which they are contained which process comprises adding a metal complexing agent to the material to form a metal complex between the ions and the complexing agent and extracting the metal complex so formed from the material as a solution in a solvent, wherein the solvent comprises at least one fluorine containing compound selected from the (hydro)fluorocarbons and the (hydro)fluorocarbon ethers.

The Patent Office

Application No: GB 9622136.1
Claims searched: 1 and 2

Examiner: C.A.Clarke
Date of search: 2 January 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C1A (AP21,AP36,AP37,AP38 APD2B,APD2S,APD2Y)

Int Cl (Ed.6): C22B 3/26

Other: ONLINE: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	US 4486391 DAINIPPON	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.